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Modification of Spill Factors Affecting Air Pollution. Volume II. The Control of the Vapor Hazard from Spills of Liquid Rocket Fuels

MSA Research Corp.
Evans City, PA

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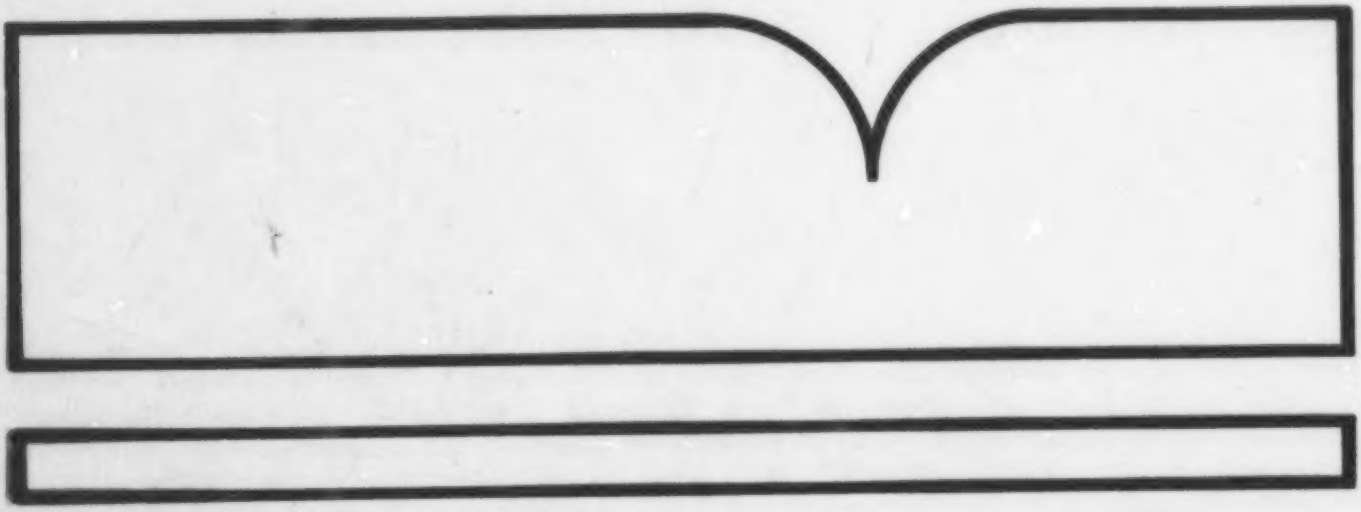

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MODIFICATION OF SPILL FACTORS AFFECTING AIR POLLUTION

Vol. II - The Control of the Vapor Hazard from Spills of Liquid Rocket Fuels

by

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16. ABSTRACT

The hypergolic rocket fuels, hydrazine and nitrogen tetroxide, are volatile hazardous materials of special interest to the Air Force. Through monitoring of ongoing Environmental Protection Agency programs, the Air Force has maintained cognizance of the developing state of the art in spill control. This Air Force supplement to the basic EPA program was a preliminary evaluation of the potential of cooling and foam covers to mitigate the vapor hazard from hydrazine and nitrogen tetroxide.

Coolants exhibited some control over vapor release from the hypergolic fuels. Liquid nitrogen was the most effective material. Logistics were deemed a major disadvantage for the anticipated spill scenarios.

Foams using commercial agents were beneficial with hydrazine but were not effective against nitrogen tetroxide. Modified foam systems incorporating acrylic resins were more effective. They were able to maintain hydrazine concentrations at or below 0.5 ppm. Some control was also exhibited with nitrogen tetroxide, but there was intermittent vapor release through the foam.

Based upon the work of this program, the acrylic foams offer a promising approach to the control of the vapor hazard from hydrazine and nitrogen tetroxide.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report addresses a preliminary evaluation of cooling and foam blankets as mechanisms of reducing the release of hazardous vapors from hypergolic rocket fuels. The results show that foam has potential for controlling the vapor release from hydrazine and nitrogen tetroxide based propellants.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

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ABSTRACT

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Foams using commercial agents were beneficial with hydrazine but were not effective against nitrogen tetroxide. Modified foam systems incorporating acrylic resins were more effective. They were able to maintain hydrazine concentrations at or below 0.5 ppm. Some control was also exhibited with nitrogen tetroxide but there was intermittant vapor release through the foam.

Based upon the work of this program the acrylic foams offer a promising approach to the control of the vapor hazard from hydrazine and nitrogen tetroxide.

The full report was submitted in partial fulfillment of Contract No. 68-03-2648, Task 9B, by MSA Research Corporation under subcontract to Rockwell International under sponsorship of the U.S. Environmental Protection Agency. This report covers the period 22 January 1980 to 4 December 1980, and work was completed as of 15 May 1981.

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ABBREVIATIONS AND SYMBOLS

AFFF	--	aqueous film forming foam
°C	--	degrees Celsius
cm	--	centimeter
°F	--	degrees Fahrenheit
g	--	gram
gal	--	gallon
in.	--	inch
min	--	minute
ml	--	milliliter
oz	--	ounce
ppm	--	parts per million
TLV	--	threshold limiting value

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SECTION 1

INTRODUCTION

Liquid rocket propellants present one class of volatile hazardous chemicals. The toxic hazard has been well recognized, and the Air Force in its facilities provides for the contingency of a spill of these materials. As the state-of-the-art in spill control has advanced, the Air Force has monitored the progress with interest for its own applications. The success of aqueous foams in controlling vapor hazards (which has been demonstrated in earlier EPA-sponsored programs) and the potential for cryogenic cooling (which was being demonstrated in this program) was justification for the Air Force to undertake an investigation of these techniques as mechanisms to control the vapor hazard from spilled rocket fuels.

The existing program was supplemented by Air Force funding for the specific purpose of investigating cooling and aqueous foam blankets to mitigate the vapor hazard of hydrazine and nitrogen tetroxide. This study was primarily a survey and was not intended to develop a total system. State-of-the-art technology was used to the fullest extent.

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SECTION 2

SUMMARY AND CONCLUSIONS

The investigation assessed the ability of two techniques -- cooling and foam covers -- to mitigate the vapor hazard of hydrazine and nitrogen tetroxide. Each technique was pursued independently for each of the propellant materials. The program used a series of laboratory tests to evaluate the various methods and materials for vapor suppression. Vapor concentrations above the two fuel materials were measured using detector tubes. Tests in which the concentrations exceeded the maximum limit of detector tubes, about 35 ppm, were considered failures.

The coolant portion of the study investigated wet ice, dry ice, liquid CO_2, and liquid nitrogen. For nitrogen tetroxide, liquid nitrogen was able to reduce the vapor concentration below the detector tube limitation. Wet ice had an immediate but small effect that persisted only as long as the ice was solid. As liquid formed, it reacted to form nitric acid. The heat of formation more than offset the cooling effects. To maintain the low vapor level, fairly large quantities of nitrogen were required, with fairly frequent make up indicated.

The adding of coolants to hydrazine reduced vapor levels below the limits of the detector tubes, but they were not able to approach the TLV. Wet ice produced the slowest reduction of vapor concentration with hydrazine. Because of the accompanying dilution, as the ice melted, the lowest vapor concentration was ultimately achieved.

The evaluation of foam systems initially considered commercially available foam agents. Representative materials of protein, fluoroportein, AFFF, and surfactant foams were selected based upon characteristics identified in a previous EPA program. A second set of materials, which covered the so-called "alcohol" or "polar solvent" foam agents, was added to these.

None of the materials selected were able to exercise any control over the vapor release rate of nitrogen tetroxide. In contrast, almost all were able to reduce substantially the vapor concentration above hydrazine. These levels varied from 2 to 20 ppm depending on the foam. The length of control also varied as a function of foam type.

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A third type of foam system was also tested. These agents were based upon acrylic modified foams previously developed by MSA which gel when used on ammonia or amine materials. The gelled foam forms a stable barrier with a low permeation of hydrazine vapor. There is some drainage which mixes with the hydrazine and gels the top liquid layer. The two layers were able to reduce the vapor concentration into the range of 0.5 ppm.

These foam formulations were also beneficial in reducing vapor release from nitrogen tetroxide. They were not able to give continuous control, however. The vapor build up beneath the foam layer resulted in intermittent vapor pulses (breathing). Although these foams were better than any other foam evaluated, they were less than desired. They did provide a basis for further development.

The acrylic modified foams tended to form a skin in contact with nitrogen tetroxide. A series of polymeric materials were tested alone and in combination with the acrylic modifier in an effort to improve the control over nitrogen tetroxide. Within the time limit of this program no major improvements over the original MSA formulations were found.

The use of coolants as a method of controlling the vapor hazard from spilled liquid hydrazine or nitrogen tetroxide is rejected. The tests showed some reduction in vapor release, but when this was equated with the volume of coolant material required and the logistics involved for projected scenarios, cooling was not deemed a viable approach.

Aqueous foam systems offered significant benefits for hydrazine. Several commercially available agents were shown to be able to reduce vapor levels to the 2 to 5 ppm range. None of the agents were effective against nitrogen tetroxide.

Acrylic modified aqueous foams developed previously for ammonia and like materials were shown to be effective for hydrazine. Foam layers reduced vapor levels to the 0.5 ppm range. These agents also had some positive effects on nitrogen tetroxide. At the conclusion of this program, these foams offered the best mechanism to control the vapor hazard from the two types of rocket propellant materials.

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SECTION 3

RECOMMENDATIONS

The prime recommendation to be made is to continue to investigate improvement in the acrylic modified foams. Although a number of modifications were tried without measurable improvement, these reflected materials which were available within the time constraints of this program.

The acrylic materials which have been used are stable primarily on the basic side. Certain other materials that exhibit better stability have been recommended by the polymer manufacturers. In addition, there is the potential for providing foams that gel on the acid side. These foams are based upon silicic acid. There has been some prior work in this area but it was for a very different application. Thus the evaluation of silicic acid gels will have to start with basics.

Certain of the potential modifications which were attempted in the test program were incompatible with the surfactant material employed in the acrylic modified formulation. This prevented their full evaluation.

Beyond the evaluation of additional materials for a nitrogen tetroxide system, there is a need to conduct some larger scale tests to fully verify the suitability of whatever foam system is selected as the best available technology. This should address the types of spill scenarios which might be encountered. Thus, at the conclusion of the test program, if results are positive, spill control systems can be designed for each scenario.

The test program should also address the clean up procedures which can or should be used after the vapor control system has been utilized.

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SECTION 4

PROGRAM PLAN

The program had as its objective the evaluation of two techniques, foam covers and surface cooling, as mechanisms to control the vapor hazard from spilled liquid rocket propellants. The planned program had three scheduled phases. Phase 1 was concerned with the evaluation of coolant technology. Phase 2 evaluated foam technology. With positive results from the first two phases a demonstration of capability was conducted as Phase 3.

The total program covered a twelve week period. The first week was used for planning and organizing the program and allowed for materials acquisition. The final two weeks were used to coordinate all information and prepare a final report. The remainder of the schedule provided for a demonstration.

PHASE 1 - COOLANT EVALUATION

This phase was scheduled for two weeks. It utilized, to the extent possible, the results of the main program on coolants. This included definition of candidates, form of application, the ratio of coolant to spilled material and the techniques for measuring vapor concentrations.

The total two weeks were spent on laboratory studies. One additional week of the program was set aside to evaluate test data and formulate conclusions and decisions.

PHASE 2 - FOAM STUDIES

This phase covered four weeks. Two weeks were devoted to evaluations of commercial agents with both hydrazine and nitrogen tetroxide. One week was given to the evaluation of the special agents proposed for test. The final week was for testing of modifications which were indicated by the test results.

The laboratory study drew upon prior work to establish candidate foam agents both commercial and special. Test procedures paralleled those successfully employed in other similar studies.

The data derived in this phase was analyzed and conclusions formulated in the same week as for the coolant data analysis.

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PHASE 3 - DEMONSTRATION

The fate of this phase depended upon the results of the first two phases. It was scheduled to cover two weeks; one week for preparation and one week for conducting the field work.

The details of the demonstration would be evolved during the course of the program through discussions with the Air Force. This would be a small scale field test encompassing a spill surface area no larger than 25 square feet. The actual test parameters depended on the mechanism selected for vapor control, foam or coolant. In either case the demonstration would parallel those used either in the main study on coolants or prior EPA work with foams. The uncertainties concerned restrictions the Air Force might want to impose to simulate real time spill scenarios.

FINAL REPORT

A final report covering all aspects of the program was submitted in draft form during the 12th week of the program.

SECTION 5

CRYOGEN EVALUATION

The use of refrigerants to cool a liquid spill and thereby reduce the equilibrium vapor pressure has been the subject of the first and main part of this program. Although the test fluids had changed for the supplemental part of the program, the basis for selecting acceptable cooling candidates was still the same. It was possible to argue for limiting the coolant to dry ice but there were circumstances which compromised that position. First, both propellant materials were soluble in or reactive with water, and second, TLVs were so low that only liquid nitrogen might be effective. It was decided initially to evaluate all four forms, but since liquid CO_2 is essentially applied as solid snow, dry ice was the only form of CO_2 evaluated.

The tests conducted were similar in all cases. The volume of propellant was 50 ml (0.01 gal) for N_2O_4 and 100 ml (0.03 gal) for hydrazine. The volume of coolant was 200 grams (7.05 oz) for both wet and dry ice and 100 ml (0.03 gal) for liquid nitrogen.

RESULTS WITH NITROGEN TETROXIDE

Wet Ice

Approximately 200 g (7.05 oz) of ice was required to provide an excess when added to 50 ml (0.01 gal) of liquid dinitrogen tetroxide. An equilibrium temperature of -10°C (14°F) was measured after one minute. The vapor concentration decreased to between 30 and 50 ppm over the liquid, after this temperature was attained.

Although some 60 minutes was required to melt all of the ice, the control of the vaporization rate was lost as soon as measurable melting of the ice had occurred. This took approximately 15 minutes. After this 15 minutes the cooling by the ice was in competition with the heat being generated by the water-N_2O_4 interaction.

Dry Ice

The addition of crushed dry ice caused agitation of the N_2O_4. The dry ice particles sank into the liquid, where they

sublimed. A dense vapor resulted that was composed of CO_2, N_2O_4 and condensed moisture. The concentration of N_2O_4 never dropped below 50 ppm even though the addition of 200 grams (7.05 oz) of dry ice was sufficient to create a continuous layer of dry ice over the N_2O_4 surface.

Liquid Nitrogen

The addition of liquid nitrogen to nitrogen tetroxide created a similar response to solid CO_2. A dense vapor cloud was released which contained red streaks indicating the carry off of N_2O_4. The addition of 100 ml (0.03 gal) of liquid nitrogen resulted in the formation of floating islands of LN_2. Solid particles which sank into the nitrogen tetroxide were observed to form at the liquid-liquid interface.

As long as excess LN_2 persisted on the surface, N_2O_4 vapor levels were suppressed into the 10-15 ppm range. As soon as the liquid nitrogen boiled off, 5-10 minutes, the N_2O_4 vapor concentration increased rapidly beyond the detection limits of detector tubes.

RESULTS WITH HYDRAZINE

Wet Ice

The addition of 200 grams (7.05 oz) of ice to hydrazine had no immediate effect. The vapor concentration did decrease slowly reaching 50 ppm, the limit of the detector tube, in about 2 minutes, and decreased to 20 ppm in ten minutes. At that time the temperature of the hydrazine-ice mixture had decreased to -3°C (27°F). These conditions persisted for about 20 minutes, which was the time necessary for melting of the ice.

Dry Ice

The application of dry ice particles to hydrazine created the same effect as for N_2O_4. There was a heavy cloud which sampling showed entrained considerable quantities of hydrazine vapor. Hydrazine levels were always above the maximum limit of the detector tubes.

Liquid Nitrogen

The liquid nitrogen-hydrazine tests also paralleled those with N_2O_4. The development of visible LN_2 on the spill surface caused a solid material to form. This material had a tendency to sink into the liquid hydrazine rather than form a floating layer.

Vapor concentrations in the range of 5 to 10 ppm were achieved as long as liquid nitrogen was maintained on the surface. When it disappeared, the vapor concentration rapidly rose to

levels beyond the limits of the detector tubes.

DATA ANALYSIS

The data showed that some reduction in the vapor hazard could be achieved with coolants. Liquid nitrogen gave the best results. In evaluating the data, consideration was given to tentative scenarios. In all cases, fast if not immediate response was necessary. The logistics of moving coolant to a spill site made that approach unattractive. On-site storage or in-place material formation was possible but both equipment costs and maintenance requirements would be very high.

It was decided on the basis of this analysis to hold up further work on this approach, pending results from the foam portion of the program. As will be seen, the foam approach was sufficiently successful that no further work was done or recommended on the coolant system.

SECTION 6

FOAM EVALUATION

Aqueous foams have seen wide use in the control of the vapor hazard from spilled hydrocarbon liquids. In the past few years there has been a number of investigations of the ability of foam to restrict the vapor hazard from a variety of spilled volatile chemicals not necessarily falling in the hydrocarbon category.

It is clear from this work that foams are effective barriers to vapor release for those chemicals which are not soluble in water. Water solubility or reactivity can affect the normal types of foam in use by the fire services, with changes in pH providing the most significant effect.

Aqueous foams are more tolerant of changes to the basic side than to the acid side. Limited work has shown that the aliphatic amines such as diethylamine can be benefited from a foam blanket. The effect is to reduce the vapor concentration above the spill, for some duration of time depending on the type of foam, the depth of the blanket and the expansion of the foam. The vapor does ultimately penetrate the blanket and the concentration above the foam will tend to reestablish an equilibrium condition.

Hydrazine is expected to behave in a similar manner. The rate of permeation through foam blankets is unknown, however, and whether standard foam systems can provide the necessary degree of control must be determined.

Efforts to use foam to control ammonia spills resulted in the development of foam systems which would gel on interaction with the ammonia. A similar action was observed with other chemicals which shifted the pH in the basic direction. Once gelled, the foam provides a greater restriction to the permeation of the gas phase. Thus these foams provided enhanced vapor mitigation.

The use of foam on spills of materials which provide an acid response has been limited to date to those materials which have a severe toxicity problem. In none of these cases is the foam able to form a blanket due to degradation by the acid action. The main purpose for foam use is a mechanism to apply water gently to reactive materials to convert the vapor to a less hazardous form: SO_3 to H_2SO_4, $SiCl_4$ to HCl, etc., and release the material as an aerosol rather than a vapor since aerosols tend to settle

out rather than disperse into the air.

One would expect N_2O_4 to behave in a similar manner. Some possibilities exist beyond normal foams. Foam solutions containing silicates can be gelled by shifting pH in the acid direction forming silicic acid. These are usually formed by slight acidulation and whether they would persist in contact with N_2O_4 is not known.

A second possibility is controlled neutralization. With chlorine bearing materials such as $SiCl_4$ with application of a foam containing NH_3(NH_4OH soln), the chlorine is reacted to NH_4Cl. This reaction occurs rapidly at the foam-chemical interface and results in a floating layer of NH_4Cl. This forms a barrier to the transfer of water in and vapor out. The reaction between the water and the chemical slows down and vapor release is sharply reduced.

There are some potential reactions with N_2O_4 which might behave in this fashion using certain hydroxides or alkali carbonates. Not all neutralization reactions behave the same way, however. NaOH solution foams are not effective against chloride materials; in fact, the reactivity becomes quite violent.

There are currently five basic foam agent types commercially available. These are proteinaceous materials derived from natural protein, aqueous film forming foam (AFFF) which employ a fluorocarbon surfactant, fluoroproteins which are combinations of AFFF and protein, synthetic materials which are hydrocarbon surfactant base, and "alcohol" or "polar solvent" agents which tend to be proprietary.

Within foam technology there are two expansion ranges in use. There are theoretical design limits but in practice the limits are 5 to 20:1 for low expansion and 250 to 750:1 for high expansion foams. Only synthetic foaming materials encompass both expansion ranges. The others are restricted to the low range. AFFF can make high expansion foam but its breakdown rate is extremely fast.

The evaluation program included representative foam agents from each category. Fluorocarbon materials perform quite poorly with water reactive materials. They are in wide use by the Air Force for fire protection. For that reason they were included.

FOAM AGENT SELECTION

Commercial Agents

In EPA-sponsored work it has been clearly shown that regardless of the type of foam, expansion or the volatile material involved, the better the water retention capability of the foam the

better is its performance. This fact was used to minimize the specific foam agents to be evaluated in the prior study. Further control of the number of test materials can be exercised by selecting a constant foam agent addition of 6 percent for low expansion. The EPA work also shows that there is little difference between 3 and 6 percent forms of the same agent from the same manufacturer.

The agents selected during prior EPA programs were selected for this program also. They are listed below. They represent the best drainage characteristics of their class.

Protein - National AeroFoam 6% Regular

Fluoroprotein - National XL 6%

Fluorocarbon - National Aero-O-Water 6%

Surfactant - MSA Ultrafoam V

The choice of the MSA agent for the surfactant candidate was made on the basis that it has the best drainage of all surfactant materials in both the low and high expansion mode and is the only surfactant agent which meets the specifications of Underwriters Laboratories for both low and high expansion foam.

In addition to these four agents, three additional agents were included. These are the Universal agent of National Foam, which reportedly is effective against ammonia; a fluorocarbon base polar solvent foam, 3M ACT; and a protein base alcohol foam, Rockwood All Purpose.

Special Agents

Three categories of special agents were included in the selected lists. Two gelling systems previously investigated by MSA for amine and ammonia were added; one using acrylic modification and the second a carboxy vinyl additive. The third category was the silicic acid system. This system is not well defined and its inclusion was as a general category.

It should be noted that as the program progressed, further modifications were made in these special agents to accommodate observed deficiencies.

TESTING OF COMMERCIAL AGENTS

Each of the selected commercial agents was carried through a screening to assess compatibility with both hydrazine and nitrogen tetroxide. All of the agents were tested in the low expansion mode. The AFFF, synthetic, fluoroprotein and the fluorocarbon polar solvent foam were also tested in the high expansion mode.

For those foams and expansion which passed the screening

test, additional tests were run to establish a basis for assessing the efficiency of vapor control. This series of tests used detector tubes to determine breakthrough times. With vapor permeation a sharp discontinuity is usually observed in vapor concentrations above the foam. This occurs when either the foam collapses completely or it becomes saturated with the vapor phase. The time to reach this point is a relative measure of the control capability of the foam blanket.

Screening Tests for Compatibility

The compatibility for each agent was determined by measuring the time necessary for the foam generated to collapse to one-half its original height. In the case of low expansion tests about 7.6 cm (3 in.) of 8 to 1 expansion foam was placed over 50 ml (0.01 gal) of the propellant material in a 500 ml (0.15 gal) beaker.

The tests with nitrogen tetroxide were easy to evaluate; all foams collapsed rapidly with only minimal control of the vaporization rate. Of the seven agents tested, the best results were obtained using MSA Type V, AFFF and 3M ACT polar solvent agent. These survived because there was some foam regeneration by the vapors being released. This action appeared to be primarily entrainment. When the foam did collapse all of the entrained vapor was released.

The tests with hydrazine had more positive results. The times for reduction to half the foam volume using low expansion foam are given in Table 1. These data do not indicate any capability in vapor suppression, only foam compatibility.

TABLE 1. THE RESULTS OF SCREENING TESTS OF LOW EXPANSION FOAMS WITH HYDRAZINE

Agent	Time Required to Obtain 1/2 Original Foam Volume (min)
National "Aero-Foam Regular"	>60
National "XL-3%"	>60
Rockwood "All Purpose"	~ 1
National Universal	>60
3M "Light Water"	~47
3M "Alcohol Solvent Concentrate"	~60
MSA Ultrafoam V	>60

Similar tests were done for the foaming agents capable of forming stable foams at higher expansion ratios. These foam samples were prepared by blowing the foaming agent solutions to form foams having expansion ratios between 100 and 150 to 1. The results were poor in all cases indicating unsuitability for the high expansion mode.

Vapor Control by Selected Commercial Agents

The five commercial agents which appeared to be compatible with hydrazine in the low expansion form were carried forward to assess their ability to block vapor release from hydrazine. It was decided there was no justification to look further at high expansion nor to do an evaluation of any commercial agent with nitrogen tetroxide.

The same test set up as was used for the compatibility tests was employed. Detector tubes were used to measure vapor concentrations above the level of the foam blanket. The best results were obtained with National Universal and MSA Type V.

Regular Protein Foam (National) --

Protein foam was compatible with hydrazine. Foam bubbles at the interface expanded as vapor was absorbed, forming a layer, which was gradually assimilated into the foam mass. The foam drained normally but the collapse rate was reduced because of regeneration by the vapors. A vapor concentration of less than 10 ppm was maintained for approximately 60 minutes by a 7 cm (~3 in.) layer of foam. Beyond this time the vapor concentration increased at a fairly rapid rate.

Fluoroprotein Foam (National) --

This foam behaved in much the same way as regular protein. Interfacial bubbles formed as vapor was assimilated and some volume expansion occurred. The level of hydrazine vapors above the foam was low, about 1 ppm, but the breakthrough time was short covering only 30 minutes. A high drainage rate caused the foam to become friable and lose its barrier effect.

Polar Solvent Foam (3M) --

The fluorocarbon based polar solvent foam was compatible with hydrazine, whereas the protein base material was not. The fluorocarbon foam behaved much like protein and fluoroprotein but there was a tendency for large bubbles to form and percolate intermittantly through the foam layer. An average vapor concentration of 20 ppm was measured for about 20 minutes after application. At that point the vapor level began a measurable increase.

Universal Foam (National) --

This agent, suitable for both normal and polar materials, followed the same pattern as all previous agents. The average vapor level above the foam blanket was 5 ppm. Breakthrough time was about 60 minutes.

Synthetic (MSA) --

Over the first 15 minutes this agent gave the best performance of all of those tested. The low expansion cover appeared to achieve complete blockage of hydrazine vapor for that period of time. After 30 minutes the vapor level had increased to 5 ppm and then maintained that level for an additional 30 minutes.

Data Clarification --

These data should be reviewed with care since there is no guarantee that the performance of these representative materials will be characteristic of all agents in that class. In fact, the opposite may be true. The selection process attempted to identify the best in each category. National Universal, 3M ACT and MSA Type V, although commercially available, are proprietary formulations not matched by other manufacturers. The data presented for these three foam agents should be treated as being unique.

The data for protein, fluoroprotein and the two materials which were eliminated during screening, AFFF and alcohol foams, can probably be taken as representative. Differences between foam agents from different manufacturers is not great in terms of drainage and chemical compatibility.

TESTING SPECIAL AGENTS

Prior work had indicated that three special foam agents might be effective against the propellant materials. Two systems have been fairly well documented in the prior work. These were systems which gelled on contact with alkaline materials. One system used an acrylic polymer and the second employed a carboxy vinyl polymer. Both systems had evolved during a program aimed at developing an effective foam system to control the vapor hazard from ammonia. The difference between the two systems concerns the rate of gellation and the stability of the gel which forms.

Both foams were very effective in controlling the vapor release from ammonia, being able to keep the concentration below the odor threshold for a measurable period of time. The similarity between ammonia and hydrazine would suggest that these foams would be effective against that material also.

The third system proposed for consideration utilized silicic

acid gels. In prior work foam systems had been defined incorporating sodium silicate (water glass) solutions. Foams formed from such solutions could be gelled by acidulation, converting the silicate to silicic acid. Several applications had been considered for this type of foam but no significant effort developed to exploit this type of system. It thus is in a more rudimentary state than the foams which gel on the alkaline side.

Testing with Hydrazine

The two gelling agents identified as MSA60 and 95 were evaluated against hydrazine in the same fashion as the commercial agents. Both materials were compatible with hydrazine. The gellation provided a stable foam mass with little collapse. Each gel eventually broke down but the effective life of the 7 cm (3 in.) layer approached four hours.

Foam 60 underwent what appeared to be a slight interaction as it was applied. The drainage formed small gel globules in the hydrazine. After ten minutes the vapor concentration above the gelled foam decreased to about 1 ppm and decreased further with time. After 30 minutes the concentration was less than 1 ppm. After several hours the gel broke down and vapor control was lost.

Foam 95 formed a gel layer more readily than Foam 60. The foam expanded slightly in the first few minutes after application rather than interacting. The drainage formed a gel layer on the surface of the hydrazine. When the gel formed, the hydrazine level above the foam was in the range of 0.5 ppm. It remained at this level for the duration of foam life. The foam did degrade but at a slower rate than Type 60 and it did not become as friable as it aged.

Testing with Nitrogen Tetroxide

As with the commercial agents, all agents selected were evaluated against both propellant materials. Both gelling foams were evaluated with N_2O_4 for compatibility. Neither material could survive against the tetroxide but they were superior to all other agents so far tested.

Type 60 reacted with nitrogen tetroxide to form a film. This provided a base upon which a foam layer can be built. This foam absorbed the vapor and underwent some expansion. The 7.6 cm (3 in.) layer was permeated in about 15 minutes. Once the foam has been fully permeated by the nitrogen tetroxide it collapses slowly taking about five minutes for full degradation. By making up the foam level intermittently or by initially using a thicker layer, some control of the vapor release can be achieved. There was not continuous release, rather the foam releases vapor in pulses. The drainage from the foam converted the N_2O_4 to nitric acid. This foam thus provided the best control of all materials

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tested to date.

Foam 95 reacted slowly with N_2O_4. There was some film formation but it was discontinuous. In general, it behaved similarly to Type 60 but did not provide the same degree of control.

Some tests were run with silicate foams. None of the systems tried were successful. The sodium silicate exaggerated the reaction between the foam and the nitrogen tetroxide which more than offset any benefit the foam might have. The formation of a silicic acid gel was never achieved. Some variations in the materials ratios of the silicates are possible, but there was not enough time to evaluate all the possible permutations of $Na_2O \cdot SiO_2$ ratios.

FOAM MODIFICATIONS

The Type 60 and 95 foams were shown to be quite effective against hydrazine with Type 95 found to be the superior foam. Against nitrogen tetroxide no foam truly was effective. Type 60 gave the best response. The fact that it tended to form a film over the surface of the tetroxide was deemed to be the basis for its control. As time allowed in the program, a variety of water soluble polymeric materials were screened to assess their capability to form a film in contact with nitrogen tetroxide. The time available in the program only permitted a cursory examination based upon visual observations of foam-nitrogen tetroxide interactions. These observations for the materials tested are tabulated in Table 2.

In the course of the screening study there were some incompatibilities between additives and surfactant materials. The major problem was a gelling reaction. For some of the promising additives to be fully evaluated it will probably be necessary to totally formulate the system optimizing the additive-surfactant combination. A beginning was made in this direction at the end of this program. It showed that surfactants based upon olefins or betaines had the best stability to nitrogen tetroxide.

FOAM-CRYOGEN COMBINATIONS

Tests were conducted to determine the effectiveness of combining cooling agents with foam systems. 3M "Alcohol Solvent Concentrate" foaming agent was chosen for these tests from among the four commercial foams that were partially compatible with N_2O_4. The foam had a life of about 15 to 20 minutes (in low expansion form), when placed directly over the liquid. When the foam was placed over tetroxide cooled with wet ice, its useful life was increased to about one hour.

Dry ice and liquid nitrogen used in combination with the "Alcohol Solvent Concentrate" foaming agent did not perform as

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TABLE 2. SCREENING OF POTENTIAL FOAM MODIFIERS

Material	Observations of Foam-Nitrogen Tetroxide Interaction
Rhoplex Acrylic Latex	Forms globular layer between foam and N_2O_4
Acrysol Acrylic Latex	Forms strands of elastomeric polymer over N_2O_4; in some cases forms an interlayer of semi-solids between the foam and N_2O_4
Polyvinyl Ether	Forms an interlayer of semi-solids between foam and N_2O_4
Polyvinyl Alcohol	Reacts with N_2O_4, but does not form an interlayer
Guar Derivatives	Reacts with N_2O_4 to form granular ppt but does not form interlayer over N_2O_4 with foams
Polyvinyl Acetate	Slow dissolution; does not retard reactions when included in foam formulations

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anticipated. The large volume of gas released by the boiling or sublimation of the coolant expanded the foam layer very rapidly. Rather than replacing the foam lost to normal collapse, this rapid expansion of the foam cover made it more susceptible to collapse from the NO_2 also being evolved. The working life of the foam remained almost unchanged when combined with dry ice and was increased very slightly when used in combination with liquid nitrogen, only when foam placement was delayed until the liquid nitrogen evaporated.

Any advantages gained by combining the effects of coolants and foam agents were only temporary since the coolant-foam system, when once applied to a spill, could not be replenished without breaking the foam cover. The combined treatment procedure thus had only a limited benefit.

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SECTION 7

PROPOSED PROGRAM CONTINUATION

HYDRAZINE VAPOR CONTROL

The Type 95 foam would appear to be an effective foam system to control the vapor hazard from hydrazine. It is necessary to expand the test size to insure that the observed behavior is not a laboratory curiosity. In conducting a scaled-up field test, conditions should be superimposed which approximate those which will exist in real time scenarios.

The test program should also consider the problems of clean up of the spill. These data, along with confirmation of the capabilities of the foam, will allow the design of a foam vapor hazard protection system for those areas where spill potential exists.

NITROGEN TETROXIDE VAPOR CONTROL

The data developed in the program so far would indicate that foam containment lies with systems which can develop a film barrier to the nitrogen tetroxide. The acrylic systems seem to have the best potential. Certain foams appear to have greater possibilities than those tested so far. They need to be mated to a compatible surfactant material for a fuller evaluation.

Some further effort in silicate systems can be justified. This should address low Na_2O materials to slow down the reaction with the tetroxide which destroyed the foams in the early tests with silicate solutions. It is possible that the silicate could be combined with the acrylic system to compliment each other.

Those suggested efforts must be first conducted within the laboratory. If a system is found which is effective, it should be carried forward to a field scale test. These tests would be the same as for hydrazine. These should include those restraints which would exist in the field and address subsequent clean up procedures. The final step, as with hydrazine, would be the design of a spill control system for the projected hazard.

The foregoing would appear to suggest separate systems for the two propellant materials. That is, of source, a possible outcome. Nitrogen tetroxide presents the most potent hazard.

Barring a major breakthrough, it is anticipated that a protective system for that material will have limitations and every step possible will be used to maximize the effectiveness.

If the system finally incorporates an acrylic material, it is possible that it would also have some degree of effectiveness against hydrazine. That possibility should be investigated. A single system effective against both materials would have definite advantages. It might be acceptable to take some penalty on the hydrazine side to have a single system. Any compromise would have to be fully analyzed but the data necessary to make this analysis should be obtained.